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# THE MECHANISM OF THE LOW-TEMPERATURE THERMAL DECOMPOSITION OF AMMONIUM PERCHLORATE

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By: Yu. P. Savnitsev, T. V. Mulina, and V. V. Boldyrev

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U. S. BOARD ON GEOGRAPHIC NAMES TRANSLITERATION SYSTEM

| Block | Italic | Transliteration | Block | Italic | Transliteration |
|---|---|---|---|---|---|
| А а | *А а* | A, a | Р р | *Р р* | R, r |
| Б б | *Б б* | B, b | С с | *С с* | S, s |
| В в | *В в* | V, v | Т т | *Т т* | T, t |
| Г г | *Г г* | G, g | У у | *У у* | U, u |
| Д д | *Д д* | D, d | Ф ф | *Ф ф* | F, f |
| Е е | *Е е* | Ye, ye; E, e* | Х х | *Х х* | Kh, kh |
| Ж ж | *Ж ж* | Zh, zh | Ц ц | *Ц ц* | Ts, ts |
| З з | *З з* | Z, z | Ч ч | *Ч ч* | Ch, ch |
| И и | *И и* | I, i | Ш ш | *Ш ш* | Sh, sh |
| Й й | *Й й* | Y, y | Щ щ | *Щ щ* | Shch, shch |
| К к | *К к* | K, k | Ъ ъ | *Ъ ъ* | " |
| Л л | *Л л* | L, l | Ы ы | *Ы ы* | Y, y |
| М м | *М м* | M, m | Ь ь | *Ь ь* | ' |
| Н н | *Н н* | N, n | Э э | *Э э* | E, e |
| О о | *О о* | O, o | Ю ю | *Ю ю* | Yu, yu |
| П п | *П п* | P, p | Я я | *Я я* | Ya, ya |

* ye initially, after vowels, and after ъ, ь; e elsewhere. When written as ё in Russian, transliterate as yё or ё. The use of diacritical marks is preferred, but such marks may be omitted when expediency dictates.

FOLLOWING ARE THE CORRESPONDING RUSSIAN AND ENGLISH

DESIGNATIONS OF THE TRIGONOMETRIC FUNCTIONS

| Russian | English |
|---|---|
| sin | sin |
| cos | cos |
| tg | tan |
| ctg | cot |
| sec | sec |
| cosec | csc |
| sh | sinh |
| ch | cosh |
| th | tanh |
| cth | coth |
| sch | sech |
| csch | csch |
| arc sin | $\sin^{-1}$ |
| arc cos | $\cos^{-1}$ |
| arc tg | $\tan^{-1}$ |
| arc ctg | $\cot^{-1}$ |
| arc sec | $\sec^{-1}$ |
| arc cosec | $\csc^{-1}$ |
| arc sh | $\sinh^{-1}$ |
| arc ch | $\cosh^{-1}$ |
| arc th | $\tanh^{-1}$ |
| arc cth | $\coth^{-1}$ |
| arc sch | $\operatorname{sech}^{-1}$ |
| arc csch | $\operatorname{csch}^{-1}$ |
| rot | curl |
| lg | log |

## GREEK ALPHABET

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Alpha | A | α | ϰ | | Nu | N | ν | |
| Beta | B | β | | | Xi | Ξ | ξ | |
| Gamma | Γ | γ | | | Omicron | O | o | |
| Delta | Δ | δ | | | Pi | Π | π | |
| Epsilon | E | ε | ϵ | | Rho | P | ρ | ϱ |
| Zeta | Z | ζ | | | Sigma | Σ | σ | ς |
| Eta | H | η | | | Tau | T | τ | |
| Theta | Θ | θ | ϑ | | Upsilon | T | υ | |
| Iota | I | ι | | | Phi | Φ | φ | ϕ |
| Kappa | K | ϰ | κ | ϰ | Chi | X | χ | |
| Lambda | Λ | λ | | | Psi | Ψ | ψ | |
| Mu | M | μ | | | Omega | Ω | ω | |

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The mechanism of the low-temperature thermal decomposition of ammonium perchlorate.

Novosibirsk.

It is known that in the course of the thermal decomposition of the crystals of ammonium perchlorate at low temperatures occurs the formation and ~~increase~~ growth of ~~embryos~~ nuclei [1, 2]. For the understanding of the mechanism of decomposition of $NH_4ClO_4$ it is necessary to know, which stages of process are connected with nucleation, and which ~~s~~ with the ~~increase~~ growth.

It is possible to consider at present established that at low temperatures the thermal decomposition of ammonium perchlorate ~~flow/lasts over~~ occurs by proton mechanism, in primary stage occurs the process of the dissociation of salt to ammonia and ~~chlorous~~ perchloric acid. The subsequent course of thermolysis is ~~joined~~ coupled with the oxidation of ammonia by the ~~decay~~ (decomposition) products of ~~chlorine kosloty~~ perchloric acid [3-6]. The majority of ~~the~~ authors ~~they~~ assume that the processes of formation and ~~increase in~~ growth of nuclei the ~~embryos~~ are caused by the course of the same ~~of the~~ stages of reaction. According to another point of view (Svetlov, Korsban; Rosser, ~~Ayacmi~~ Isaacmi, Wise, ~~Vays~~) along with the course of the indicated reactions during thermal decomposition of $NH_4ClO_4$ occurs also the formation of substances, capable of entering into ~~the~~ interaction with

ammonia or solid ammonium perchlorate [7, 8]. In this case the growth of nuclei (process) increase in the embryos can go, also, without the course of the stage of dissociation.

We have made the proposition that the nucleation occurs as a result of the course of the primary stage of the dissociation of salt and subsequent secondary reactions, and the growth of nuclei but an increase in the embryos is caused by the oxidation-reduction reactions of the active oxidizers ($HClO_4$ and the oxides of calorine), being regenerated in the course of process. For the check of the (expressed propositions) was studied the effect of a number of factors on the processes of formation and growth of increase in the nuclei embryos.

In work used single, mono, crystals oil $NH_4ClO_4$, obtained by the evaporation vaporization of the aqueous solution of salt of quality brand "chemically pure" at room комнатну temperature. The investigated crystal was placed under microscope into (a) special furnace and in the course of reaction was taken photograph. Temperature was not more than 235° C. According to the obtained negatives (was determined) to the time future of the appearance of the first nucleus embryo (induction period), (were) calculated the

rates of formation and ~~increase in~~ growth of the ~~embryos~~ nuclei.

For the solution to the assigned task was used the method of ~~dopirovaniya~~ doping. During introduction to crystal $NH_4ClO_4$ of the additions of bivalent cations occurs the formation of ~~supplementary~~ additional cation vacancies.

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In this case because of the presence in the crystals of proton conductivity [9] and of the possibility of the transmission of proton to significant distances [5] will be increased the rate of the process of dissociation. The additions of bivalent anions must increase the number of anionic vacancies, ~~conduct~~ leading to diminution in the quantity of being present in crystal cation vacancies and to the slow down of the rate of dissociation of $NH_4ClO_4$.

If the stage of dissociation is responsible for formation and ~~increase in~~ growth of the ~~embryos~~ nuclei, then bivalent additions must affect the rate of both processes. But if dissociation does not play the significant

role in the course of ~~an increase in~~ growth of the ~~embryos~~ nuclei, then the indicated additions will affect only the rate of their growth. In this case cation additions will increase rate of ~~nuclei forming~~ nucleation, and anionic - decrease.

It was established that the ~~doping effective~~ doping by ions $Cu^{++}$ and $Sr^{++}$ increases rate of ~~nuclei forming~~ nucleation, ~~but~~ and by ions $Cr_2O_7^{--}$ - ~~it~~ decreases. In this case additions $Cu^{++}$ and $Sr^{++}$ do not affect the rate of growth of ~~embryos~~ nuclei. Addition $Cr_2O_7^{--}$ increases the rate of growth, which can be caused by the catalytic influence of the generated during reaction oxides of chromium. Thus, by the method of ~~dopirovaniya~~ doping it is shown that the dissociation does not play the significant role in the course of ~~an increase in~~ the growth of ~~embryos with~~ nuclei during thermolysis [10, 11]. If the made conclusion ~~probably~~ is correct then the ammonia, introduced into reaction vessel, must differently affect formation and ~~increase in~~ growth the ~~embryos~~ nuclei. At atmospheric pressure the ~~decay~~ (decomposition) rate of ammonium perchlorate, which takes place by proton mechanism, is proportional to the equilibrium pressure of the vapors of perchloric acid [12]. Therefore one should expect the linear dependence of the rate of ~~formation of embryos~~ nucleation on

the partial equilibrium pressure of perchloric acid in system. If the developed point of view about the difference in the mechanisms of formation and growth is accurate, then this dependence must not be observed for the rate of growth of nuclei. The obtained results confirmed proposition about the fact that the dissociation of salt was important only for nucleation, and was not essential for the (nuclei) growth. Actually, the rate of nucleation decreases in proportion to an increase in the partial pressure of ammonia (according to the) hyperbolic law, and the rate of growth (according to the) linear. The rate of nucleation increases linearly in proportion to the increase in the partial pressure of perchloric acid in system [10], the calculated (by the) known equilibrium constant of the process of the dissociation of salt [13].

Thus, it is established that the mechanisms of formation and growth of nuclei are different. To this testify also the discovered by us differences in the activation energy of these processes (activation energy of formation is equal to 50 kcal/mole, the activation energy of growth 10 kcal/mole). Consequently, the process of nucleation is caused by the course of the reaction of

dissociation and subsequent secondary reactions, ~~but~~ and the process of growth is connected in essence with the secondary reactions, in the course of which occurs the regeneration of the products, which facilitate the oxidation of solid salt.

~~the~~ fact, which confirms the expressed point of view, is also the predominance ~~preponderance~~ of ~~an increase in~~ the ~~embryos~~ ~~above~~ emergence ~~with the~~ thermolysis of the ammonium salts, formed by acid-oxidizers ($NH_4ClO_3$, $NH_4BrO_3$, $NH_4IO_3$), and the absence of ~~an increase in~~ the growth of ~~embryo~~ ~~with~~ nucleus during the thermolysis of the salts, formed by the acids, not capable of oxidizing ammonia ($NH_4Cl$, $NH_4HCO_3$) [10, 11]. Assumption about the fact that in process of the development of reaction zone ~~the~~ a significant role play the generated ~~ing~~ in reaction oxides of chlorine is confirmed by the fact of the acceleration of nucleation in the crystals of ammonium perchlorate, (preliminarily) exposed ~~persistent~~ in ~~the~~ an atmosphere of ~~dioxide~~ dioxide of chlorine - one of reaction gases. Actually, of the crystals, exposed ~~persistent~~ 20 min in the atmosphere with the partial pressure of the dioxide of chlorine equal to 3 torr, time of the formation of the (nucleus) growing at linear speed ~~embryo~~ is reduced to 12 min

at ~~with~~ 230° C (for the untreated crystals this time is equal to 30 min).

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Thus, it is established that the process of nucleation during thermal decomposition of $NH_4ClO_4$ is connected with the course of the reaction of the dissociation of salt and subsequent secondary reactions. In the process of ~~an increase in~~ growth of the ~~embryos~~ nuclei occur the secondary reactions of the interaction of solid salt with those which are being regenerating in the course of process by oxidizers. Dissociation of $NH_4ClO_4$ does not play in this case ~~of~~ a significant role.

The process of nucleation can be presented in the following form. Thermal dissociation during the decomposition of salt occurs both on external and on internal surface. The latter can be formed by the pores, which are hollow dislocation cores, which emerge on surface. During the diffusion ~~directions~~ at the forming in the pores ~~of~~ ammonia and perchloric acid to external crystal ~~boundary~~ surface occurs the accumulation of the excess of perchloric acid as a result of its ~~less~~ lower diffusion

rate, which leads to the initiation of the process of decomposition.

Nucleation during thermolysis of $NH_4ClO_4$ begins under surface [2], since here are more favorable than the stacking conditions for accumulation of perchloric acid. The separation efficiency of the components of gaseous mixture depends, other conditions being equal, on the diameter of pore.

Consequently, the important role in the course of nucleation must play dislocations with the determined value and the orientation of Burgers's vector. To investigation of the role of dislocations during thermolysis of $NH_4ClO_4$ are dedicated a number of articles [14, 15]. However, until now, the question remains not solved why in the process of nucleation is active only one thousanth of the dislocations, which are present in the initial crystal. Probably this is caused by the favorable stereochemical arrangement of dislocations, analogous with that which was revealed by Thomas for the carbonate of calcium [16].

For the explanation of the role of dislocations together with Thomas and Williams we studied the dislocation structure of ammonium perchlorate. Investigations were conducted by the method of optical microscopy using interferential contrast. It

was established that in the process of the sublimation of salt most active are ~~Burgers~~ screw dislocations, which can serve as indication of their important role in the process of nucleation.

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